

# VibHam

An Efficient Program for Predicting Rovibrational Spectra of Diatomic Molecules

Version 1.0

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## FAQ - Frequently Asked Questions

### How do install VibHam on Linux/MacOS/Windows?

VibHam is available for Linux, Windows, and Mac OS X platforms. To download the necessary python files, please visit our GitHub repository: <https://github.com/gmccarve/VibHam>. Within our GitHub repository are instructions on how to copy the repository, test the installation of VibHam, and utilize example potential energy and dipole moment curves to get an understanding of how VibHam is run.

### I've installed VibHam, how do I run it?

Upon the successful installation of VibHam, the program can be either used interactively with a graphical user interface (GUI) or through a text-based output. To access the GUI, use one of the following commands:

```
python3 /path/to/VibHam.py -i
```

```
python3 /path/to/VibHam.py -Interactive
```

```
python3 /path/to/GUI.py
```

To utilize the text-based output format, a data file must be specified using the *-Data* flag and either the atoms or the masses must be specified using the *-Atoms* or *-Masses* flags. For example, to utilize a potential energy curve of HF found in the data file *HF.txt*, the following command would be used:

```
python3 /path/to/VibHam.py -Data HF.txt -Atoms H F
```

The GUI offers a more in-depth examination of the rovibrational properties of diatomic molecules than is afforded by the text-based program. This includes plotting capabilities, the access to data tables, and the ability to view the constructed wavefunctions.

## **What do I need to run VibHam?**

In order to run the VibHam program, all of the python files in the GitHub repository are required as well as an installation of Python 3.7 or newer. Four non-standard python libraries are required to run VibHam: NumPy, pandas, matplotlib, and PyQt5. The latter three are required only for GUI. To install these Python libraries, it is recommended to use the *pip* installation command (see: <https://pypi.org/project/pip/>).

## **How do I cite VibHam?**

A manuscript for the VibHam program is currently being completed and so following a successful peer review process, we will have a citation available.

## **How do I make a recommendation or suggestion for VibHam?**

Please email Gavin McCarver at [gmccarve@vols.utk.edu](mailto:gmccarve@vols.utk.edu) for recommendations or suggestions.

## **Can I help contribute to the further development of VibHam?**

Please email Gavin McCarver at [gmccarve@vols.utk.edu](mailto:gmccarve@vols.utk.edu) for opportunities to help the further development of VibHam.

## **What further developments are planned for VibHam?**

Two further developments are planned for VibHam: multithreaded processing to make the construction of the Hamiltonian matrices more efficient and moving beyond diatomic molecules to more complex vibrational modes.

# 1 General Information

## *1.1 Program Components*

VibHam consists of several separate programs that are called as necessary during each run. The following files and modules are included in the current version of VibHam:

Atoms.py	-	Isotopic mass information
Conversions.py	-	Conversion factors
GUI.py	-	Main program of graphical user interface
Hamil.py	-	Constructs Hamiltonian matrices
Input.py	-	Input program
Interpolate.py	-	Interpolate the energy and dipole curves
Spectra.py	-	Calculate spectroscopic values
VibHam.py	-	Main program for text-based output
Windows.py	-	Program used for external windows in the GUI

## 2 Calling the Program

The VibHam program is called in the same manner as other Python scripts and codes using the *python* or *python3* command.

Upon the successful installation of VibHam, the program can be either used interactively with a graphical user interface (GUI) or through a text-based output. To access the GUI, use one of the following commands:

```
python3 /path/to/VibHam.py -i
```

```
python3 /path/to/VibHam.py -Interactive
```

```
python3 /path/to/GUI.py
```

To utilize the text-based output format, a data file must be specified using the *-Data* flag and either the atoms or the masses must be specified using the *-Atoms* or *-Masses* flags. For example, to utilize a potential energy curve of HF found in the data file *HF.txt*, the following command would be used:

```
python3 /path/to/VibHam.py -Data HF.txt -Atoms H F
```

The GUI offers a more in-depth examination of the rovibrational properties of diatomic molecules than is afforded by the text-based program. This includes plotting capabilities, the access to data tables, and the ability to view the constructed wavefunctions.

### 3 Input Arguments

The VibHam text-based output allows for fine control of the program using several input arguments or parameters. The only input arguments that are required for each run of VibHam are *-Data* and either *-Atoms* for the identity of the two atomic species or *Masses* for the mass value of each species. The latter allows for the examination of two-body systems that are not strictly diatomic molecules. In this case, some of the output information becomes meaningless such as the spectroscopic constants and Dunham parameters. Each input argument is initiated by adding

‘*-\$INPUT \$VALUE*’

after the VibHam.py file is called. Here, *\$INPUT* corresponds to the input argument (italicized in the list below) and *\$VALUE* corresponds to the value(s) to be assigned to *\$INPUT*. Some of the input arguments require one value to be included, some require two values, and some require none. The latter are Boolean style arguments where the presence of the *-\$INPUT* argument causes a flag to change from *False* to *True* within the VibHam program.

Argument	Description	Type	Number of inputs	Options	Default
Data	The name of the file to be read in by VibHam. Must be in either two or three columns: 1 - Bond distance values 2 - Energy values 3 - Dipole moment values (optional)	Str	1	-	-
R_unit	Unit for bond distance values.	Str	1	‘ang’, ‘bohr’, ‘m’	‘ang’
E_unit	Unit for energy values.	Str	1	‘hartree’, ‘kj/mol’, ‘kcal/mol’, ‘ev’, ‘j’, ‘cm’	‘hartree’
Dip_Unit	Unit for dipole moment values.	Str	1	‘debye’, ‘au’	‘debye’
Atoms	Atoms used for the potential energy curve. Up to element 118 is implemented.	Str	2	-	-
Masses	Masses of the atoms to be used in the calculation. Must be given in atomic mass units.	Float	2	-	-
Isotopes	Isotope values to use. Must match with the dictionary found in Atoms.py. Must match order of Atoms.	Int	2	Depends on atom type	0

Energy_Fit	Degree for power series expansion for the energy curve.	Int	1	2, 4, 6, 8, 10, 12, 14, 16	2
Dipole_Fit	Degree for power series expansion for the dipole curve	Int	1	0 – 11	0
EigVal	Convergence value for truncation of the Hamiltonian Matrix in wavenumbers.	Float	1	-	0.1
J	Maximum value for the rotational quantum number.	Int	1	-	0
Trap	Number of intervals for trapezoid rule for numerical integration.	Int	1	-	2000
v	Maximum value for the vibrational quantum number	Int	1	-	20
Print	Level of printing: 1 - Print only converged eigenvalues 2 - Print only converged eigenvalues/vectors 3 - Print all eigenvalues 4 - Print all eigenvalues/vectors	Int	1	1 – 4	1
Charge	Charge of molecule	Int	1	-	0
InterPoints	Number of grid points to include in the energy and dipole curve interpolation.	Int	1	-	100000
Constants	Number of spectroscopic constants to calculate for a given state.	Int	1	-	3
LoadData	Attempt to load precomputed Hamiltonian Matrices	Boolean	1	True, False	False
Interactive	Load the GUI	Boolean	1	True, False	False
i	Load the GUI	Boolean	1	True, False	False

**Table 3.1** List of input arguments.

## 4 Program Sub-blocks

### 4.1 Initial Interpolation of Potential Energy Curve

The initial interpolation of the potential energy curve uses a standard polynomial (Eq. 4.1) to

$$V(R) = c_m R^m + c_{m-1} R^{m-1} + c_{m-2} R^{m-2} + \dots c_1 R^1 + c_0 \quad (4.1)$$

determine three values: the equilibrium bond length ( $R_e$ , Å), the energy at the equilibrium bond length ( $E_{min}$ ,  $E_H$ ), and the equilibrium rotational constant ( $B_e$ ,  $\text{cm}^{-1}$ ) based on Eq. 4.2. An iterative process is followed that interpolates the potential energy curve using successively more terms in the polynomial expansion: first with a 0<sup>th</sup> order (constant) function, then by a 1<sup>st</sup> order (linear) function, 2<sup>nd</sup> order (quadratic) function, and so on. Once the process is complete (up to either the 11<sup>th</sup> order or an order equal to one less than the number of data points in the datafile), the function with the lowest overall error is determined and used to find the previously mentioned values. The equilibrium bond length is calculated numerically using a grid of points along the potential energy curve while the energy at the equilibrium bond length is found using the polynomial expansion itself.

$$\frac{h}{8\pi^2 \mu R_e^2} \quad (4.2)$$

### 4.2 Power Series Expansion of the Potential Energy Curve

Following the determination of  $R_e$  and  $E_{min}$ , the potential energy curve is shifted to remove any dependence on the 0<sup>th</sup> and 1<sup>st</sup> order terms for the power series expansion (Eq. 4.3) which can take any even order ( $n$ ) from 2 up to 16. The requirement for an even order puts the restriction that the

$$V(\zeta) = c_n \zeta^n + c_{n-1} \zeta^{n-1} + c_{n-2} \zeta^{n-2} + \dots c_2 \zeta^2, \quad \zeta = R - R_e \quad (4.3)$$

power series expansion terms much approach  $\infty$  at both  $\zeta = \pm \infty$ . The potential energy curve is interpolated using the power series expansion at the given order and then the error of the

interpolation is determined. This includes the determination of the mean absolute deviation (MAD, Eq. 4.4), root mean squared error (RMSE, Eq. 4.5), and coefficient of determination (COD, Eq. 4.6).

$$\frac{1}{N} \sum_{i=1}^N |E_i^{Fit} - E_i^{Ab initio}| \quad (4.4)$$

$$\sqrt{\frac{1}{N} \sum_{i=1}^N (E_i^{Fit} - E_i^{Ab initio})^2} \quad (4.5)$$

$$1 - \frac{\sum_{i=1}^N (E_i^{Fit} - E_i^{ab initio})^2}{\sum_{i=1}^N (\bar{E} - E_i^{ab initio})^2}, \quad \bar{E} = \frac{1}{N} \sum_{j=1}^N E_j^{ab initio} \quad (4.6)$$

Following the interpolation of the potential energy curve, the  $c_2$  term of the power series expansion can be used to calculate the force constant ( $k$ , Eq. 4.7), the harmonic frequency ( $\nu$ , Eq. 4.8), the vibrational constant ( $\omega_e$ , Eq. 4.9), and the  $\beta$  value (Eq. 4.10). Here,  $\mu$  is the reduced mass of the system,  $c$  is the speed of light in cm/s, and  $\hbar$  is the reduced Planck constant. In Eq. 4.10, the  $10^{10}$  multiplier is used to convert from  $\text{m}^{-1}$  to  $\text{\AA}^{-1}$ . The vibrational constant and the  $\beta$  value are used in the following section to construct the harmonic and anharmonic Hamiltonian matrices.

$$k = 2c_2 \quad (4.7)$$

$$\nu = \sqrt{\frac{k}{\mu}} \quad (4.8)$$

$$\omega_e = \frac{\nu}{2\pi c} \quad (4.9)$$

$$(4.10)$$



$$\beta = \frac{\sqrt[4]{k\mu}}{\sqrt{\hbar}} \cdot 10^{10}$$

The choice in the order of the power series expansion has a large effect on several aspects of the VibHam program. Shown in Table 4.1 is the error of the power series fit (MAD and COD) and change in the vibrational constant for CO using the potential energy curve of Shi *et al.* The potential energy curve is fit exactly using an 8<sup>th</sup> order power series as seen by the COD value of 1 with a mean absolute deviation of less than 1  $\mu\text{E}_\text{H}$ . The change in the vibrational constant is no greater than 0.1  $\text{cm}^{-1}$  between an 8<sup>th</sup> order and 16<sup>th</sup> order power series and thus, and thus an 8<sup>th</sup> order power series function is recommended for the potential energy curve of Shi *et al.*

**Table 4.1** Comparison of the mean absolute deviation, coefficient of determination, and vibrational constant for the  $^{12}\text{C}^{16}\text{O}$  isotopologue as a function of the size of the expansion in the power series fit for the potential energy curve of Shi *et al.*<sup>1</sup> The experimentally determined vibrational constant for the  $^{12}\text{C}^{16}\text{O}$  isotopologue is 2169.8232  $\text{cm}^{-1}$ .<sup>2</sup>

Order of Power Series Expansion	Mean Absolute Deviation ( $\text{E}_\text{H}$ )	Coefficient of Determination	Predicted $\omega_e$ ( $\text{cm}^{-1}$ )
2	$2.45 \cdot 10^{-2}$	0.385077	1745.1809
4	$9.9 \cdot 10^{-4}$	0.999507	2233.3577
6	$1.8 \cdot 10^{-5}$	0.999999	2166.2107
8	$6.4 \cdot 10^{-7}$	1.000000	2168.8456
10	$5.9 \cdot 10^{-7}$	1.000000	2168.7844
12	$4.1 \cdot 10^{-7}$	1.000000	2168.7689
14	$3.1 \cdot 10^{-7}$	1.000000	2168.7872
16	$2.2 \cdot 10^{-7}$	1.000000	2168.8083

### 4.3 Power Series Expansion of the Dipole Moment Curve

The power series expansion for the dipole moment curve is similar to that for the potential energy curve except the power series is not truncated at the quadratic term. Similar error metrics (Eq. 4.4-4.6) are determined for the power series interpolation of a given order and the equilibrium dipole moment ( $\mu_e$ ) is likewise determined.

For charged, isotopically labelled diatomic molecules, the dipole moment curve must be shifted to properly account for the changes in the system. To do that, the dipole moment curve is shifted according to changes in the mass of the isotopically labelled atoms (Eq. 4.11) where  $M'$  corresponds to the change in the ratio of the atomic masses,  $M_n^{standard}$  is the mass of the most abundant isotope for atom  $M_n$  and  $M_n^{labelled}$  is the mass of the isotopically labelled atom. For a positively charged, diatomic molecule, the dipole moment curve ( $D$ ) is shifted ( $D'$ ) according to Eq. 4.12 to more positive values whereas negatively charged, isotopically substituted diatomic molecules have their dipole moments shifted to more negative values.

$$M' = \frac{M_1^{Standard}}{M_2^{Standard}} - \frac{M_1^{Labelled}}{M_2^{Labelled}} \quad (4.11)$$

$$D' = D \pm \zeta \cdot M' \quad (4.12)$$

### 4.4 Construction of Hamiltonian Matrices

The main function of the VibHam program depends on the construction of between one and four Hamiltonian matrices. The first involves the harmonic portion of vibrational motion while the second involves the anharmonic portion. The two additional matrices include a centrifugal potential Hamiltonian matrix which accounts for the rotational nature of a diatomic molecule and a transition dipole moment Hamiltonian matrix which is used to calculate the intensity of rovibrational excitations. Each of these matrices is discussed below.

#### 4.4.1 Harmonic Hamiltonian Matrix

The purely harmonic portion of the vibrational nature of a diatomic can be captured using Eq. 4.13 where  $\hbar$  is the reduced Planck constant,  $\omega$  is the vibrational constant (Eq. 4.9), and  $v$  is the vibrational quantum number. The resulting harmonic vibrational Hamiltonian matrix ( $H_{HO}$ ) is populated only on the diagonal. The diagonalization of this matrix would yield energy levels as if the vibrational Schrödinger equation was solved within the HO approximation. Thus, the energy levels would be evenly spaced and no coupling between vibrational states would be observed.

$$H_{HO}[v, v] = \frac{1}{2} \hbar \omega (2v + 1) \quad (4.13)$$

#### 4.4.2 Anharmonic Hamiltonian Matrix

In order to move beyond the HO approximation, the higher order power series expansion coefficients of Eq. 4.3 are utilized. The anharmonic vibrational Hamiltonian matrix ( $H_{AO}$ ) is constructed according to Eq. 4.14 below, as a sum over the expansion coefficients ( $c_n$ ) from the power series fit of the PEC (Eq. 4.3). Here, the *bra* and *ket* correspond to the HO wavefunctions with the vibrational quantum numbers  $v$  and  $v'$ , respectively, as a function of the dimensionless variable  $q$ . The explicit forms of the HO wave functions are shown in Eq. 4.15 where  $N^v$  is the normalization constant (shown in Eq. 4.16) and  $H^v$  are the Hermite polynomials. The integrals for the Anharmonic Hamiltonian matrix are solved analytically using the expression shown in Eq. 4.17.

$$H_{AO}[v, v'] = \sum_3^n \langle \Psi_{HO}^v(q) | c_n q^n | \Psi_{HO}^{v'}(q) \rangle, \quad q = \beta \xi \quad (4.14)$$

$$\Psi_{HO}^v = N^v H^v(q) e^{-q^2/2} \quad (4.15)$$

$$N^v = \frac{1}{\sqrt[4]{\pi}} \frac{1}{\sqrt{2^v v!}} \quad (4.16)$$

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{(2n)!}{n! 2^{2n+1}} \sqrt{\frac{\pi}{a^{2n+1}}}, \text{ for } a > 0 \quad (4.17)$$

#### 4.4.3 Centrifugal Potential Hamiltonian Matrix

In order to properly account for the quantized rotational nature of a vibrating diatomic molecule, a centrifugal potential barrier is introduced.<sup>3</sup> This barrier introduces a  $1/R_e^2$  term as a function of the chosen rotational state ( $J$ ) and is shown explicitly in Eq. 4.18. A Hamiltonian matrix is constructed similar to the anharmonic matrices discussed previously where the HO wave functions are utilized but now in terms of  $x$  and not the dimensionless variable  $q$ . A tensor ( $H_{cent}^J$ ) is constructed from this matrix as a function of the rotational quantum number (Eq. 4.19) which includes a  $J(J+1)$  term. The integrals of Eq. 4.18 are solved numerically using the trapezoid rule. Through testing, we have found that truncating the integrals between  $\pm 0.9 \cdot R_e$  with 2000 intervals in between results in stable and accurate values.

$$H_{cent}[v, v'] = \left\langle \Psi_{HO}^v(x) \left| \frac{1}{(x + R_e)^2} \right| \Psi_{HO}^{v'}(x) \right\rangle \quad (4.18)$$

$$H_{cent}^J = H_{cent} \frac{\hbar^2 J(J+1)}{2\mu} \quad (4.19)$$

#### 4.4.4 Total Hamiltonian Matrix

Once the harmonic, anharmonic, and centrifugal potential barrier matrices have been constructed, they are then added together and diagonalized in order to predict several properties of the diatomic molecule such as the energy levels, wave functions, transition energies, classical turning points along the PEC for each energy level, and the error associated with the finite size of the total Hamiltonian matrix. The wave functions that are constructed are then visualized and stored for later use alongside the transition dipole moments (discussed below).

#### 4.4.5 Stability of Total Matrix

Numerical instabilities have been observed for the anharmonic Hamiltonian matrix due to the possibility of very large numbers from the factorials of Eq. 4.17. The instabilities have been observed for cases above  $v = 37$  and so the VibHam program performs an automatic check of the total Hamiltonian matrix for said instabilities. To do this, the total Hamiltonian matrix is diagonalized and the eigenvalues are evaluated. If a negative eigenvalue is found, then the total Hamiltonian matrix is truncated by a value of one, rediagonalized, and then analyzed again. This process is repeated until no negative eigenvalues are found.

#### 4.4.6 Truncation Error of Finite Hamiltonian Matrices

The total Hamiltonian matrix is a finite size matrix and so the theoretical limit of an infinite number of basis sets (the harmonic oscillator wave functions) is not possible. Because of this, some vibrational states will not be well described using the finite basis and there will be some inherent error in the eigenvalues and eigenvectors. To approximate this error, the VibHam program will truncate the size of the matrix by a value of one, diagonalize this new matrix, and examine the difference in the eigenvalues between the true and truncated matrices. If no difference is calculated between the two matrices for a specific vibrational state, then we assume that that state has been converged and is well described with the given, total matrix. The error of each vibrational state increases as  $v$  increases with the highest vibrational state having an infinite error due to it being removed from the truncated matrix. These errors are printed alongside each vibrational state in the output. An internal check is performed so that eigenvalues with truncation errors below a given threshold (controlled through the *EigVal* command line argument) are considered to be converged while all others are not. The VibHam program will always print information relevant to the converged state, but in order to view the non-converged states or the to view the eigenvector contributions, higher integers for the *Print* command line argument must be used. To help illustrate the truncation error associated with the finite size of the total Hamiltonian matrix, Table 4.2 shows the first three eigenvalues for the  $^{12}\text{C}^{16}\text{O}$  isotopologue using the potential energy curve of Shi *et al.*<sup>1</sup> as a function of the size of the total Hamiltonian matrix. In order to approximate a converged ground state energy, a maximum  $v$  value of seven must be used. For each excited state,  $v$  must be increased by a value of three in order to reach a converged energy. This check for the truncation error is performed for all J-states.

**Table 4.2** Comparison of the first three eigenvalues ( $E_0$ ,  $E_1$ ,  $E_2$ ) as a function of the size of the Hamiltonian matrix for the  $^{12}\text{C}^{16}\text{O}$  isotopologue using the potential energy curve of Shi *et al.*<sup>1</sup> Values shown in  $\text{cm}^{-1}$ . A 12<sup>th</sup> degree power series expansion is used for the PEC

$v_{\text{max}}$	$E_0$	$E_1$	$E_2$
0	1091.0476	-	-
1	1083.1325	3294.2592	-
2	1083.1290	3232.2055	5570.2907
3	1081.4152	3231.5448	5368.7942
4	1081.3725	3224.6531	5362.6161
5	1081.3724	3223.9230	5344.9261
6	1081.3678	3223.9040	5340.4798
7	1081.3676	3223.8671	5340.1733
8	1081.3676	3223.8615	5339.9739
9	1081.3676	3223.8612	5339.9189
10	1081.3676	3223.8610	5339.9135
11	1081.3676	3223.8610	5339.9106
12	1081.3676	3223.8610	5339.9106
13	1081.3676	3223.8610	5339.9105
14	1081.3676	3223.8610	5339.9105
15	1081.3676	3223.8610	5339.9105

#### 4.4.7 Transition Dipole Moment Hamiltonian Matrix

The transition dipole moment (TDM) Hamiltonian Matrix is constructed first from a power series fit of the dipole moment function (DMF) which takes a form similar to that of Eq. 4.3 except the power series includes the constant and linear terms. Following the fit of the DMF, the TDM is constructed in a form similar to the anharmonic Hamiltonian Matrix where the expansion coefficients ( $c_\gamma$ ) of the DMF are utilized with the HO wave functions. These matrix elements are shown in Eq. 4.20, below. These integrals are solved analytically using Eq. 4.17.

$$TDM[v, v'] = \sum_0^v \langle \Psi_{HO}^v(q) | c_\gamma q^\gamma | \Psi_{HO}^{v'}(q) \rangle \quad (4.20)$$

#### 4.4.8 Oscillator Strength and Einstein A Coefficients

Once the TDM matrix has been constructed, the intensity of each rovibrational excitation can be calculated using the corresponding anharmonic wave functions of the initial ( $\psi$ ) and final ( $\psi'$ ) rovibrational states, shown in Eq. 4.21. A dot product is performed between the eigenvectors of the initial state and the TDM matrix and then a second dot product is performed between the resulting column vector and the eigenvectors of the final state. This value can then be converted to both an oscillator strength ( $f$ , Eq. 4.22) and an Einstein A coefficient ( $A$ , Eq. 4.23) to make easier comparisons with experimental data. Here,  $m_e$  is the electron rest mass,  $e$  is the charge of an electron,  $\omega$  is the transition energy, and  $S$  is the Hönl-London Factor.<sup>4</sup>

$$T = \langle \psi | TDM | \psi' \rangle \quad (4.21)$$

$$f = \frac{8\pi m_e \omega S_{J''}^{J'} T^2}{3h^2 e^2 2J' + 1} \quad (4.22)$$

$$A = \frac{64\pi^4 \omega^3 S_{J''}^{J'} T^2}{3h^4 c^3 2J' + 1} \frac{1}{4\pi\epsilon_0} \quad (4.23)$$

#### 4.5 Energy Levels and Turning Points

The total Hamiltonian matrix is diagonalized to determine the eigenvalues and eigenvectors. The eigenvectors are used to calculate the intensity of different rovibrational excitations (discussed below) while the eigenvalues are used to calculate different properties such as turning points and spectroscopic constants (discussed below). The VibHam program prints the eigenvalues for each converged rovibrational state alongside the error associated with that state (see section 4.4.6) and information related to the turning points. The turning points are calculated by determining where each rovibrational state crosses the potential energy curve on both the left- and right-hand sides. This is only performed within the bounds of the given potential energy curve even though the interpolated curve could be utilized. This choice was made so as to eliminate any error that may be associated with the interpolated curve beyond the bounds of the given curve. In addition to the left- and right-hand turning points, the center point between them is also printed in the output file. This section of the output of the VibHam program is outlined and described in Figure 4.1, below. The eigenvalues calculated are stored as a two-dimensional array where the first dimension is based on the J-value and the second dimension is the eigenvalues at that given J-value.

```

*****
These are the converged energy levels and their respective turning points:

On the J = 5 surface

State      Energy (cm^-1)      Error      ΔE      LEFT TP      RIGHT TP      CENTER
4          17409.460923      1.114000e-02      3437.852223      0.7135231      1.3278815      0.7135231
3          13971.608699      1.900000e-04      3599.924949      0.7301294      1.2641594      0.7301294
2          10371.683751      0.000000e+00      3766.576855      0.7510612      1.1975794      0.7510612
1           6605.106895      0.000000e+00      3938.839899      0.7791762      1.1251293      0.7791762
0           2666.266997      0.000000e+00           0.000000      0.8238203      1.0372314      0.8238203

On the J = 4 surface

State      Energy (cm^-1)      Error      ΔE      LEFT TP      RIGHT TP      CENTER
4          17234.562655      1.013000e-02      3444.998378      0.7142955      1.3246374      0.7142955
3          13789.564277      1.700000e-04      3607.235178      0.7311336      1.2607609      0.7311336
2          10182.329099      0.000000e+00      3774.083528      0.7522297      1.1940264      0.7522297
1           6408.245571      0.000000e+00      3946.544499      0.7808754      1.1211129      0.7808754
0          2461.701072      0.000000e+00           0.000000      0.8270643      1.0318247      0.8270643

On the J = 3 surface

State      Energy (cm^-1)      Error      ΔE      LEFT TP      RIGHT TP      CENTER
4          17094.370065      9.380000e-03      3450.721962      0.7149134      1.3220113      0.7149134
3          13643.648103      1.600000e-04      3613.090794      0.7319059      1.2581347      0.7319059
2          10030.557309      0.000000e+00      3780.096712      0.7532239      1.1912458      0.7532239
1           6250.460596      0.000000e+00      3952.716072      0.7822657      1.1179461      0.7822657
0          2297.744524      0.000000e+00           0.000000      0.8298449      1.0274221      0.8298449

On the J = 2 surface

State      Energy (cm^-1)      Error      ΔE      LEFT TP      RIGHT TP      CENTER
4          16989.065518      8.850000e-03      3455.018547      0.7154541      1.3200031      0.7154541
3          13534.046970      1.500000e-04      3617.486855      0.7324466      1.2560493      0.7324466
2           9916.560115      0.000000e+00      3784.611185      0.7539963      1.1890831      0.7539963
1           6131.948930      0.000000e+00      3957.349366      0.7833471      1.1154744      0.7833471
0          2174.599565      -0.000000e+00           0.000000      0.8319304      1.0240236      0.8319304

On the J = 1 surface

State      Energy (cm^-1)      Error      ΔE      LEFT TP      RIGHT TP      CENTER
4          16918.786143      8.520000e-03      3457.884797      0.715763      1.31869      0.715763
3          13460.901346      1.400000e-04      3620.419638      0.7328328      1.2547362      0.7328328
2           9840.481708      0.000000e+00      3787.623019      0.7545369      1.1876156      0.7545369
1           6052.858689      0.000000e+00      3960.440428      0.7841195      1.1139297      0.7841195
0          2092.418261      0.000000e+00           0.000000      0.8333979      1.0217064      0.8333979

On the J = 0 surface

State      Energy (cm^-1)      Error      ΔE      LEFT TP      RIGHT TP      CENTER
4          16883.623531      8.350000e-03      3459.318480      0.7159175      1.3180721      0.7159175
3          13424.305051      1.400000e-04      3621.886652      0.7330645      1.2540411      0.7330645
2           9802.418399      0.000000e+00      3789.129592      0.7547687      1.1869204      0.7547687
1           6013.288806      0.000000e+00      3961.986619      0.7845057      1.11308      0.7845057
0          2051.302187      0.000000e+00           0.000000      0.8341703      1.0205478      0.8341703

*****

```

**Figure 4.1** Segment of the output from the VibHam program which shows the eigenvalues for each converged vibrational state on each rotational surface. The first column is the vibrational state followed by the energy, truncation error, and difference in energy between the next lowest state. The last three columns show the left and right turning points (TP) followed by the center of the energy curve at that state. These values are based on the HF potential energy curve of Coxon *et al.*<sup>5</sup>



## 4.6 Dissociation Energy

The VibHam program calculates an approximate dissociation energy (both  $D_0$  and  $D_e$ ) using the difference between the minimum energy at the equilibrium bond length and the energy at the longest given bond length. This value is only approximate, however, as the longest bond length may not correspond to the dissociation limit. In this case, we include an error calculated as the difference in energy at the two longest bond lengths. For potential energy curves which include information at the dissociation limit, this error value is (near) zero and so the dissociation energy is calculated with a higher degree of accuracy. The  $D_e$  value is corrected for using the zero point energy (ZPE) which is defined as the energy of the  $J=0, v=0$  state to determine the  $D_0$  value.

```
*****
Dissociation Energy

De
    0.106274 +/- 0.014320 Eh
    2.891873 +/- 0.389654 eV
    66.688091 +/- 8.985622 kcal/mol
    23324.513548 +/- 3142.769000 cm^-1

D0
    0.096928 +/- 0.014320 Eh
    2.637544 +/- 0.389654 eV
    60.823128 +/- 8.985622 kcal/mol
    21273.211362 +/- 3142.769000 cm^-1

*****
```

**Figure 4.2** Segment of the output from the VibHam program which shows the approximate dissociation energy (both  $D_0$  and  $D_e$ ) in different units. The second column of values is the error of the dissociation calculated as the different in energy between the two longest bond lengths of the given potential energy curve. These values are based on the HF potential energy curve of Coxon *et al.*<sup>5</sup>

## 4.7 Rovibrational Excitations

Using the rovibrational eigenvalues and intensity values (Eqs. 4.121-4.23), each possible rovibrational excitation can be examined. The VibHam program considers all vibrational excitations between converged states (see sec. 4.4.6) and rotational excitations with a  $\Delta J$  value of  $\pm 1$ . Shown in Figure 4.3 is a portion of the output of the rovibrational excitations. Note that large Hamiltonian matrices and high J-values result in a large number of excitations being printed. For convenience sake, the excitations are subdivided according to the vibrational transition.

```
*****
```

Vi	Ji	Vj	Jj	Ei	Ej	$\Delta E$	TDM	f	A
0	0	0	1	2051.302187	2092.418261	41.116075	-1.824707e+00	6.436141e-05	2.418834e-02
0	1	0	0	2092.418261	2051.302187	-41.116075	-1.824707e+00	-2.145380e-05	-7.256502e-02
0	1	0	2	2092.418261	2174.599565	82.181304	-1.825104e+00	8.579947e-05	2.318784e-01
0	2	0	1	2174.599565	2092.418261	-82.181304	-1.825104e+00	-5.147968e-05	-3.864641e-01
0	2	0	3	2174.599565	2297.744524	123.144959	-1.825765e+00	1.157939e-04	8.365065e-01
0	3	0	2	2297.744524	2174.599565	-123.144959	-1.825765e+00	-8.270992e-05	-1.171109e+00
0	3	0	4	2297.744524	2461.701071	163.956547	1.826692e+00	1.469770e-04	2.049466e+00
0	4	0	3	2461.701071	2297.744524	-163.956547	1.826692e+00	-1.143154e-04	-2.635028e+00
0	4	0	5	2461.701071	2666.266997	204.565925	1.827884e+00	1.785196e-04	4.076438e+00
0	5	0	4	2666.266997	2461.701071	-204.565925	1.827884e+00	-1.460615e-04	-4.982313e+00
0	0	1	0	2051.302187	6013.288806	3961.986620	-9.185544e-02	1.571631e-05	1.645338e+02
0	0	1	1	2051.302187	6052.858689	4001.556502	-8.920941e-02	1.497194e-05	5.329583e+01
0	1	1	0	2092.418261	6013.288806	3920.870545	9.451625e-02	5.489111e-06	1.688367e+02
0	1	1	1	2092.418261	6052.858689	3960.440428	9.186968e-02	5.238350e-06	5.479739e+01
0	1	1	2	2092.418261	6131.948931	4039.530669	8.657727e-02	9.490198e-06	6.196790e+01
0	2	1	1	2174.599565	6052.858689	3878.259124	-9.719269e-02	6.889565e-06	1.151841e+02
0	2	1	2	2174.599565	6131.948931	3957.349365	-9.189813e-02	3.142502e-06	3.282183e+01
0	2	1	3	2174.599565	6250.460596	4075.861031	-8.395810e-02	8.104452e-06	6.413762e+01
0	3	1	2	2297.744524	6131.948931	3834.204406	9.988557e-02	7.707824e-06	1.058008e+02
0	3	1	3	2297.744524	6250.460596	3952.716072	9.194072e-02	2.244095e-06	2.338357e+01
0	3	1	4	2297.744524	6408.245571	4110.501047	8.135093e-02	7.308186e-06	6.405206e+01
0	4	1	3	2461.701071	6250.460596	3788.759525	1.025957e-01	8.332986e-06	1.025694e+02
0	4	1	4	2461.701071	6408.245571	3946.544499	9.199734e-02	1.744829e-06	1.812447e+01
0	4	1	5	2461.701071	6605.106895	4143.405824	-7.875476e-02	6.712223e-06	6.287957e+01
0	5	1	4	2666.266997	6408.245571	3741.978574	1.053238e-01	8.870738e-06	1.012491e+02
0	5	1	5	2666.266997	6605.106895	3938.839899	-9.206785e-02	1.426985e-06	1.476504e+01

**Figure 4.3** Segment of the output from the VibHam program which shows the first ten pure rotational excitations on the  $v=0$  surface and the first seventeen vibrational and rovibrational excitations between the  $v=0$  and  $v=1$  surfaces. The first four columns show the initial vibrational ( $V_i$ ) and rotational states ( $J_i$ ), the final vibrational ( $V_j$ ) and rotational states ( $J_j$ ). The next columns show the energy (in  $\text{cm}^{-1}$ ) of the initial state ( $E_i$ ), the energy of the final state ( $E_j$ ), and the excitation energy ( $\Delta E$ ) followed by the value of the transition dipole moment matrix element, the  $f$ -value, and Einstein coefficient for the excitation. These values are based on the HF potential energy curve of Coxon *et al.*<sup>5</sup> and the HF dipole moment curve of Li *et al.*<sup>6</sup>

## 4.8 Spectroscopic Constants

By solving truncated or expanded forms of Eqs. 4.24, 4.25, and 4.26, the various vibrational, rotational, and rovibrational spectroscopic constants can be calculated. As the VibHam program stores the energy levels as a function of the vibrational and rotational states separately, Eq. 4.24 can be solved to calculate the vibrational spectroscopic constants on different rotational states and Eq. 4.25 can be solved to calculate the rotational constants on different vibrational states. Thus, the  $G$  and  $F$  expressions include  $j$  and  $v$  superscripts to indicate that the constants are on a given rotational or vibrational state, respectively. The  $H$  expression is applied to the rovibrational energy levels to calculate the different vibration-rotation coupling constants and overall equilibrium rotational and vibrational constants.

$$G_v^J = \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + \omega_e y_e \left( v + \frac{1}{2} \right)^3 + \omega_e z_e \left( v + \frac{1}{2} \right)^4 + \dots \quad (4.24)$$

$$F_j^v = B_e J(J+1) - D_e [J(J+1)]^2 + H_e [J(J+1)]^3 + \dots \quad (4.25)$$

$$\begin{aligned} H_{vj} = & \omega_e \left( v + \frac{1}{2} \right) - \omega_e x_e \left( v + \frac{1}{2} \right)^2 + \dots \\ & + B_e J(J+1) - D_e [J(J+1)]^2 + \dots \\ & - \alpha_e \left( v + \frac{1}{2} \right) (J+1) + \gamma_e \left( v + \frac{1}{2} \right)^2 (J+1) - \beta_e \left( v + \frac{1}{2} \right) (J+1)^2 + \dots \end{aligned} \quad (4.26)$$

```

*****
Pure Vibrational Constants on Different J-Surfaces

      J = 0      J = 1      J = 2      J = 3
we    4.151672e+03  4.278592e+03  4.532275e+03  4.912408e+03
wexe  -9.959849e+01 -2.001484e+02 -4.011244e+02 -7.022798e+02
weye   2.926662e+00  2.527548e+01  6.994563e+01  1.368823e+02

      J = 4      J = 5
we    5.418524e+03  6.049998e+03
wexe  -1.103245e+03 -1.603528e+03
weye   2.260032e+02  3.371991e+02

```

**Figure 4.4** Segment of the output from the VibHam program which shows the first three vibrational constants ( $\omega_e$ ,  $\omega_e x_e$ , and  $\omega_e y_e$ ) on the first six rotational surfaces. These values are based on the HF potential energy curve of Coxon *et al.*<sup>5</sup>

```

*****
Pure Rotational Constants on Different v-Surfaces

      v = 0      v = 1      v = 2      v = 3
Be    2.056228e+01  1.978907e+01  1.903567e+01  1.830206e+01
De   -2.119873e-03 -2.064779e-03 -2.010044e-03 -1.958046e-03
Fe    1.633013e-07  1.587110e-07  1.546163e-07  1.485820e-07

      v = 4
Be    1.758513e+01
De   -1.911443e-03
Fe    1.428791e-07

```

**Figure 4.5** Segment of the output from the VibHam program which shows the first three rotational constants ( $B_e$ ,  $D_e$ , and  $F_e$ ) on the first five vibrational surfaces. These values are based on the HF potential energy curve of Coxon *et al.*<sup>5</sup>

```

*****
Vibrational Constants on the Full Surface

Constant          cm^-1          MHz
we                4.151672e+03    1.244640e+09
wexe              -9.959849e+01    -2.985888e+07
weye              2.926662e+00     8.773913e+05

Rotational Constants on the Full Surface

Constant          cm^-1          MHz
Be                2.095631e+01    6.282543e+06
De                -2.147556e-03    -6.438211e+02
Fe                1.657823e-07     4.970029e-02

Rotation-Vibration Coupling Constants (cm^-1)

          v = 1          v = 2
J = 1      -7.930159e-01    9.904918e-03
J = 2       5.545525e-05    -1.802168e-07
J = 3      -5.085838e-09     2.478089e-10

Rotation-Vibration Coupling Constants (MHz)

          v = 1          v = 2
J = 1      -2.377402e+05    2.969420e+03
J = 2       1.662507e+01    -5.402765e-02
J = 3      -1.524696e-03     7.429123e-05

```

**Figure 4.6** Segment of the output from the VibHam program which shows the first three vibrational constants ( $\omega_e$ ,  $\omega_{ex_e}$ , and  $\omega_{ey_e}$ ), first three, rotational constants ( $B_e$ ,  $D_e$ , and  $F_e$ ), and the six vibration-rotation coupling constants calculated on the full rovibrational surface. These values are based on the HF potential energy curve of Coxon *et al.*<sup>5</sup>

## 4.9 Dunham Coefficients

The last sub-block that runs for the VibHam program is to fit the potential energy curve to a Dunham-type polynomial.<sup>7</sup> This polynomial was developed specifically to calculate the spectroscopic constants of diatomic molecules and takes the form shown in Eq. 4.27. The polynomial expansion coefficients ( $a_n$ ) are then used to calculate the Dunham Y-parameters which have spectroscopic equivalents (Table 4.3).

$$V(\chi) = hca_0\chi^2 * (1 + a_1\chi + a_2\chi^2 + \cdots a_6\chi^6),$$
$$\chi = \frac{\xi}{R_e}, \quad a_0 = \frac{\omega_e^2}{4B_e} \quad (4.27)$$

**Table 4.3** Spectroscopic Equivalents for the Dunham Y-parameters.

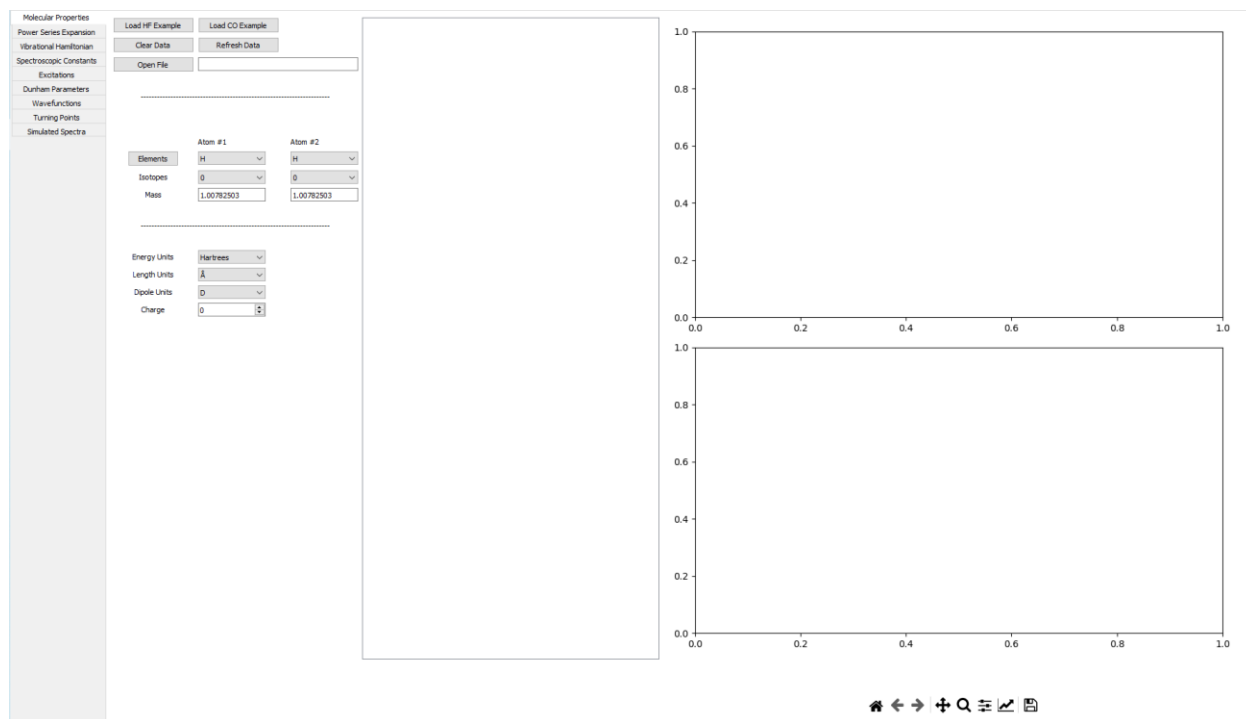
Dunham Y-parameters	Spectroscopic Equivalent
$Y_{01}$	$B_e$
$Y_{02}$	$D_e$
$Y_{03}$	$F_e$
$Y_{04}$	$H_e$
$Y_{10}$	$\omega_e$
$Y_{20}$	$\omega_e X_e$
$Y_{30}$	$\omega_e Y_e$
$Y_{40}$	$\omega_e Z_e$
$Y_{11}$	$\alpha_e$
$Y_{12}$	$\beta_e$
$Y_{21}$	$\gamma_e$

## 5 Graphical User Interface

The graphical user interface (GUI) for the VibHam program contains nine tabs which separates different parts of the program into related sections. Each of the nine tabs is described in more detail in the following subsections and are located on the left side of the application. Please note that the layout and usability of VibHam does not change across operating systems but the application may look slightly different. Each of the figures used in the following sections were produced on a Windows 10 machine.

### 5.1 Molecular Properties Tab

The first screen that appears when VibHam is opened is the *Molecular Properties* tab (Figure 5.1). This tab is used to load and manipulate the potential energy and dipole moment curves. The *Molecular Properties* tab is subdivided into three columns. The leftmost columns allows the user to load a datafile, choose the atom types, and choose the units of the input data, the second shows a data table of the input data, and the third shows plots of the energy and dipole curves.



**Figure 5.1** *Molecular Properties* Tab of the VibHam program.

The leftmost column of the *Molecular Properties* tab is shown to the right in figure 5.2. The functionality for each item in the tab is described below:

-----

	Atom #1	Atom #2
Elements	H	H
Isotopes	0	0
Mass	1.00782503	1.00782503

-----

Energy Units	Hartrees
Length Units	Å
Dipole Units	D
Charge	0

**Load HF Example** – Load an example using the potential energy curve of Coxon *et al.*<sup>5</sup> and the dipole moment curve of Li *et al.*<sup>6</sup> for HF. Shortcut – “Ctrl + L”

**Load CO Example** - Load an example using the potential energy curve of Shi *et al.*<sup>1</sup> for CO.

**Clear Data** – Clear the internal bond length, energy, and dipole moment arrays. Note that this button only affects the *Molecular Properties* tab and does not automatically cascade to affect the other tabs.

**Refresh Data** – Refresh the internal bond length, energy, and dipole moment arrays. Used following changes in the *checked/unchecked* behavior of the internal data table (see *Data Table*, below). Shortcut – “Ctrl + R”

**Open File** – Open a file explorer window to choose an input file. Shortcut – “Ctrl + O”

**Elements** – Open an interactive periodic table of elements to choose atom types (Figure 5.3).

**Atom type drop-down menus** – Assign the identity of one of the two atom types. Listed in order of the periodic table.

**Isotope drop-down menus** – Assign the isotope for a given atom. Changes based on atom type. Isotope 0 is the most abundant isotope for that atom.

**Mass** – Mass of the given atom. Changes based on chosen isotope. Can be manually overwritten to be any mass in AMU.

**Energy Units drop-down menu** – Assign the units for the potential energy based on input file.

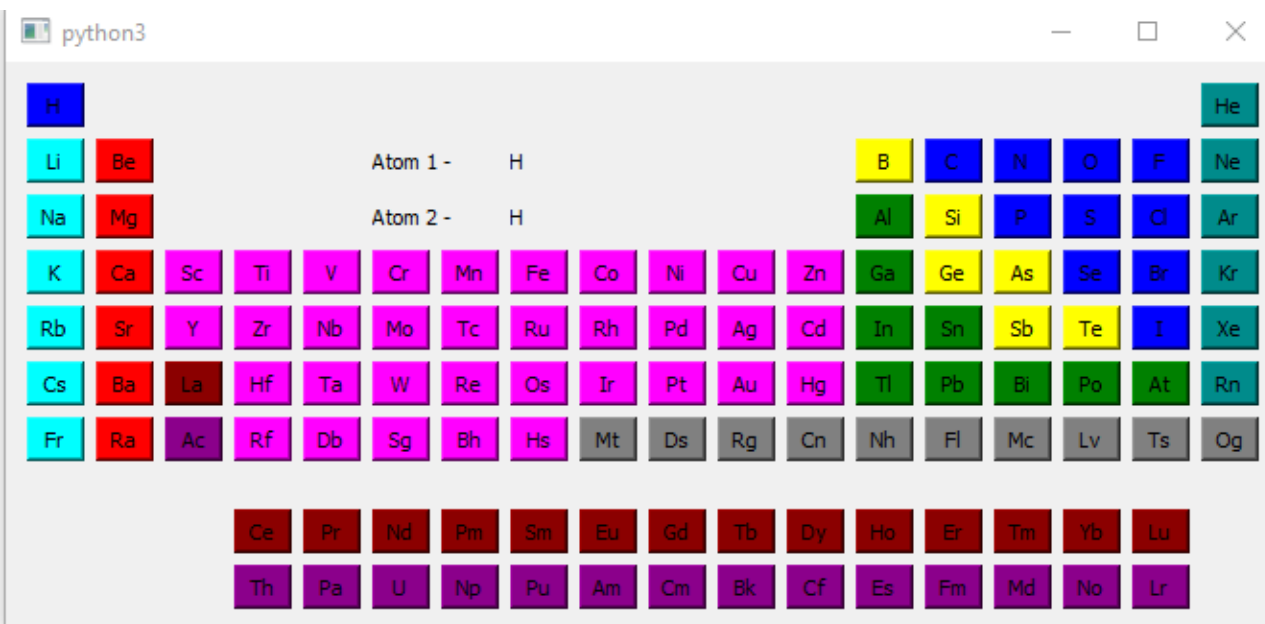
**Length Units drop-down menu** – Assign the units for the bond length based on input file.

**Dipole Units drop-down menu** – Assign the units for the dipole moment.

**Charge drop-down menu** – Assign the charge of the system.

**Figure 5.2** Leftmost column of the *Molecular Properties* Tab.





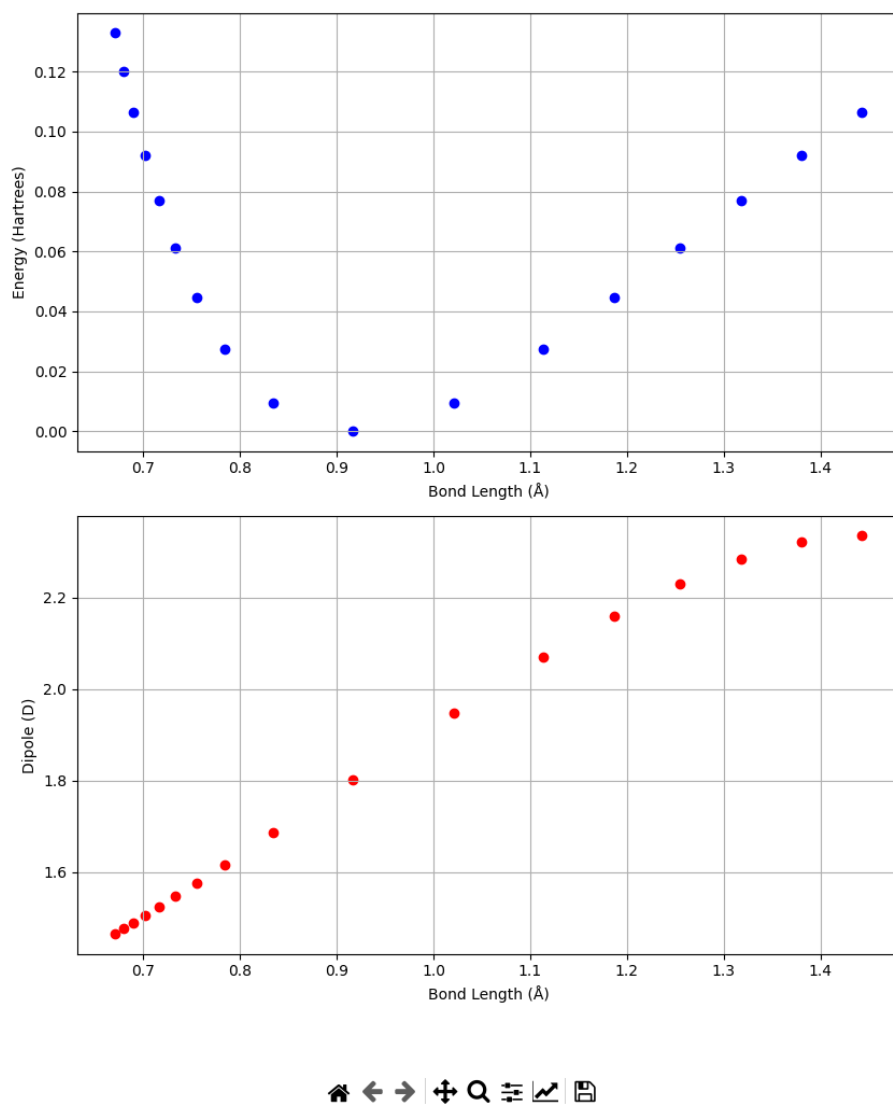
**Figure 5.3** The interactive periodic table to define atom types.

The middle section of the *Molecular Properties* tab (Figure 5.4) is an internal data table for the input data. There are 3-4 columns for the table: *R* (bond length information), *E* (energy information), *D* (dipole moment information, optional), and *Include?*. The last column is used if a user wishes to omit certain rows in the data table by unchecking the checkbox. The internal arrays of the R/E/D data does not update automatically when a checkbox is unchecked and so the user must click the *Refresh Data* button discussed earlier in order to update the internal arrays.

	R	E	D	Include?
1	0.670501	0.132811906252478	1.46467473876697	<input checked="" type="checkbox"/>
2	0.67949	0.119891140022581	1.47625609812407	<input checked="" type="checkbox"/>
3	0.689796	0.106274120103192	1.48964352667848	<input checked="" type="checkbox"/>
4	0.70176	0.091954608870457	1.50532307288529	<input checked="" type="checkbox"/>
5	0.715901	0.076921903491338	1.52403492702714	<input checked="" type="checkbox"/>
6	0.733063	0.061162275725756	1.54698417681151	<input checked="" type="checkbox"/>

**Figure 5.4** Upper portion of the data table found in the middle of the *Molecular Properties* tab. Data shown is that of the HF potential energy and dipole curve of Coxon *et al.*<sup>5</sup> and of Li *et al.*<sup>6</sup>

The right-most column of the *Molecular Properties* tab involves two plots: one for the potential energy curve and one for the dipole moment curve (Figure 5.5). The units for each plot change according to the drop-down boxes discussed previously. The plots are made using the matplotlib.pyplot library and so all of the functionality afforded to standalone plots can be utilized here. The eight-item toolbar below the plots is the matplotlib.pyplot toolbar and allows for some manipulation of the plots. Each plot is updated following the *Refresh Data* button.



**Figure 5.5** Plots of the potential energy curve (upper portion) of Coxon *et al.*<sup>5</sup> and the dipole moment curve (lower portion) Li *et al.*<sup>6</sup> for the HF diatomic molecule.

## 5.2 Power Series Expansion Tab

The *Power Series Expansion* tab has a similar layout as the previous tab in that there are three sections of objects. The first section (Figure 5.6) involves manipulating the interpolation of the energy and dipole curves using a power series expansion. Below is a description of each of the objects in this section of the tab:

**Power Series Order** – Choose the order of the power series expansion for the energy curve (left) and dipole curve (right). Automatically interpolates each curve upon a change in the value.

**Interpolation Points** – Choose the number of points to use to interpolate the energy curve (left) and dipole curve (right). The value affects the accuracy of the predicted equilibrium constants (see below). Automatically interpolates each curve upon a change in the value.

**Interpolate the Energy and Dipole Curves** – This button interpolates each curve at the given order using the given number of interpolation points.

**Power Series Coefficients** – This button opens an external window to view the power series coefficients for the energy curve (left) and dipole curve (right).

**Mean Absolute Error** – Mean absolute error for the power series expansion for the energy curve (left) and dipole curve (right).

**Root Mean Squared Error** – Root mean squared error for the power series expansion for the energy curve (left) and dipole curve (right).

**Coefficient of Determination** – Coefficient of determination for the power series expansion for the energy curve (left) and dipole curve (right).

**Display Error Values** – Open an external window to view the error values for the power series expansion.

	Energy	Dipole
Power Series Order	8	5
Interpolation Points	10000	10000
Interpolate the Energy & Dipole Curves		
Power Series Coefficients	Energy	Dipole
Mean Absolute Error		
Root Mean Squared Error		
Coefficient of Determination		
Display Error Values	Energy	Dipole
Plot Interpolated Data	Energy	Dipole

---

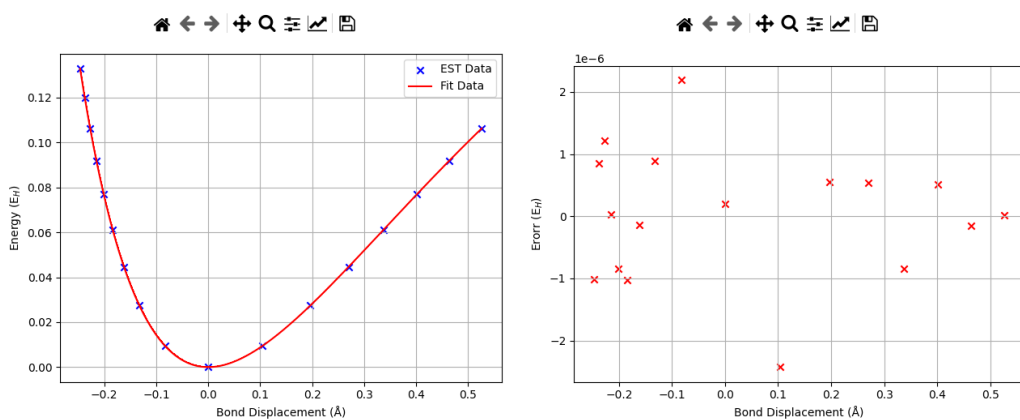
Equilibrium Constants	
Bond Length	
Minimum Energy	
Vibrational Constant	
Rotational Constant	
Dipole Moment	

**Figure 5.6** Left-hand side *Power Series Expansion* tab.

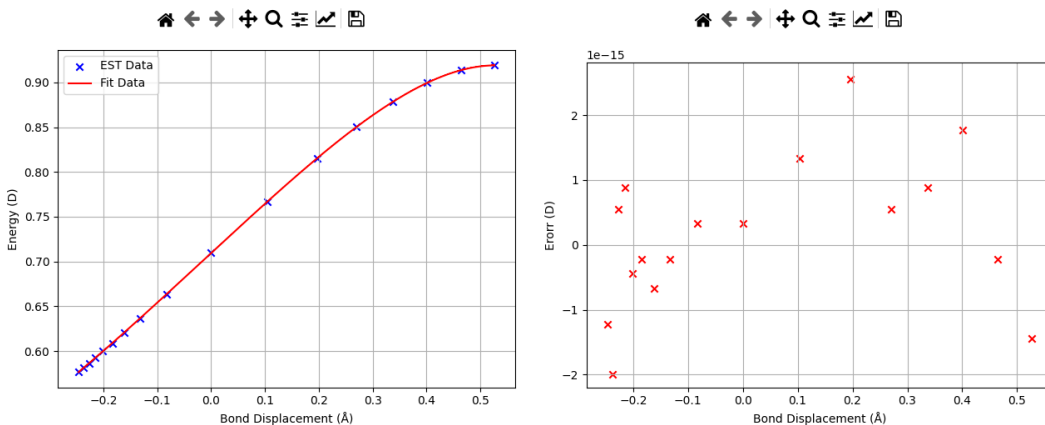
*Plot Interpolated Data* – Change the plots on the right of the screen to view either the interpolated energy curve (left) or dipole curve (right). The energy curve is automatically plotted following each interpolation.

*Equilibrium Constants* - Lists the predicted equilibrium constants that can be calculated using the interpolated energy and dipole curves.

The plot at the center of the *Power Series Expansion* tab is that of either the interpolated energy or dipole curve (Figure 5.7-5.8). The blue crosses indicate the given data points while the red line indicates the interpolated curve. The plot on the right of the tab is the error associated with the interpolation of each given data point.



**Figure 5.7** Plots of the interpolated energy curve (left) and error of interpolation (right) for the HF diatomic molecule using the potential energy curve of Coxon *et al.*<sup>5</sup>



**Figure 5.8** Plots of the interpolated dipole curve (left) and error of interpolation (right) for the HF diatomic molecule using the dipole curve of Li *et al.*<sup>6</sup>

### 5.3 Vibrational Hamiltonian Tab

The left-hand side of the *Vibrational Hamiltonian* tab allows the user to control the construction of the different Hamiltonian matrices required for the VibHam program. Each object is described below and is shown in Figure 5.9.

Maximum $v$ value	<input type="text" value="25"/>
Maximum $J$ value	<input type="text" value="10"/>

---

Harmonic Matrix	<input type="button" value="Generate"/>	<input type="button" value="View"/>	<input type="button" value="Save"/>
Anarhmonic Matrix	<input type="button" value="Generate"/>	<input type="button" value="View"/>	<input type="button" value="Save"/>
Centrifugal Matrix	<input type="button" value="Generate"/>	<input type="button" value="View"/>	<input type="button" value="Save"/>
Transition Dipole Moment Matrix	<input type="button" value="Generate"/>	<input type="button" value="View"/>	<input type="button" value="Save"/>
All Matrices	<input type="button" value="Generate"/>	<input type="button" value="View"/>	<input type="button" value="Save"/>

---

---

Calculate Highest Converged State?	<input type="button" value="Yes"/>
Maximum Truncation Error	<input type="text" value="0.01"/>

---

**Figure 5.9** Left-hand side of the *Vibrational Hamiltonian* tab for the VibHam program.

*Maximum  $v$  value* – This value controls the size of the Hamiltonian matrices. The chosen value results in  $v+1$  sized matrices.

*Maximum  $J$  value* – This value controls the number of  $J$ -surfaces to examine. This value only affects the centrifugal potential and total matrix.

*Generate* – Each of the five generate buttons instructs the VibHam program to make the requested Hamiltonian matrix. The last generate button constructs all of the matrices while the other four only generate

*View* – Each of the five view buttons instructs the VibHam program to open an external window displaying the requested Hamiltonian matrix. The last generate button shows the total Hamiltonian matrix while the other four only show the individual matrices.

*Save* – Each of the five save buttons instructs the VibHam program to save the requested Hamiltonian matrix to an external *.npy* file. The last generate button saves the total Hamiltonian matrix while the other four only save the individual matrices.

*Check Stability of Total Matrix* – This buttons performs a check of the total Hamiltonian matrix to ensure that no negative eigenvalues are produced. Performing this check truncates the total Hamiltonian matrix to the maximum size identified to not produce negative eigenvalues. See section 4.4.5. This check is only performed on the  $J = 0$  surface.

*Calculate Highest Converged State?* – This button examines the truncation error due to the finite size of the total Hamiltonian matrix on all J-surfaces. The total Hamiltonian matrix is not truncated. Clicking the *Yes* button opens an external window showing the highest converged state on every J-surface and a prompt asking to view the truncation errors. If the *Yes* button in this dialog box is clicked, an external data table is opened that shows the truncation error for every eigenvalue on all J-surfaces. If the *No* button in this dialog box is clicked, the dialog box is closed.

*Maximum Truncation Error* – This value is the user defined cutoff value for the truncation error. All eigenvalues with truncation errors below this value are assumed to be converged. Value in  $\text{cm}^{-1}$ .

*View Eigenvectors* – This button opens an external dialog box where the user can choose to view the eigenvectors on all available J-surfaces.

*View Contributions* – This button opens an external dialog box where the user can choose to view the square of the eigenvectors on all available J-surfaces.

*Refresh Eigenvalues* – This button refreshes the eigenvalues that are displayed to the right of the *Vibrational Hamiltonian* tab. As the centrifugal matrix has a  $J(J+1)$  component, it only needs to be computed once for a given  $v$  value. Thus, when the maximum  $J$  value changes, the eigenvalues on different J-surfaces can easily be recomputed and displayed using this button.

*Eigenvalues data table* – The data table to the right of the *Vibrational Hamiltonian* tab lists the eigenvalues in order for a purely harmonic system (only using the harmonic Hamiltonian matrix) and then the true, anharmonic eigenvalues on each available J-surface.

## 5.4 Spectroscopic Constants Tab

The *Spectroscopic Constants* tab allows the user to calculate, view, and plot vibrational constants on different J-surfaces (left-hand column and bottom-left plot) and rotational constants on different v-surfaces (central column and bottom-right plot). Rovibrational constants are shown in the right-hand column.

The *Order* row in the vibrational column controls how many constants are calculated and displayed: 0<sup>th</sup> order calculates only  $\omega_e$ , 1<sup>st</sup> order calculates  $\omega_e$  and  $\omega_e x_e$ , and so on. The *Plot* row controls which constant is plotted below the table. The right-hand data table displays the predicted vibrational constants up to the given order on all available J-surfaces. See section 4.8 for mathematical details.

The *Refresh* button re-reads the total Hamiltonian matrix used to calculate and plot the different spectroscopic constants.

The *Order* row in the rotational column controls how many constants are calculated and displayed: 0<sup>th</sup> order calculates only  $B_e$ , 1<sup>st</sup> order calculates  $B_e$  and  $D_e$ , and so on. The *Plot* row controls which constant is plotted below the table. The center data table displays the predicted rotational constants up to the given order on all available v-surfaces. If the truncation errors are previously determined (see section 5.3) then values only up to converged v-surface are calculated.

The right-hand data table displays the rovibrational spectroscopic constants as functions of different v and J contributions. For examples, v = 0 and J = 1 displays the 0<sup>th</sup> order rotational constant  $B_e$  whereas v = 1 and J = 1 displays the rovibrational coupling constant  $\alpha_e$ . The number of rovibrational constants that are calculated are based on both the vibrational and rotational *Order* values previously mentioned.

See section 4.8 for mathematical details.

## 5.5 Excitations Tab

The *Excitations* tab consists of three buttons and a data table (Figure 5.10). Each of the buttons controls the sorting of the excitations either for pure vibrational excitations (left-hand button), pure rotational excitations (center button), or rovibrational excitations (right-hand button). The data table lists the initial ( $V_i, J_i$ ) and final ( $V_j, J_j$ ) quantum numbers, the initial energy level ( $E_i, \text{cm}^{-1}$ ), final energy level ( $E_j, \text{cm}^{-1}$ ), transition energy ( $dE, \text{cm}^{-1}$ ), transition dipole moment matrix elements (TDM, atomic units), the oscillator strength/f-value ( $f, \text{s}^{-1}$ ), and the Einstein A-coefficient ( $A, \text{s}^{-1}$ ). See section 4.7 for further information.

Sort by Vibrational Excitations					Sort by Rotational Excitations			Sort by Rovibrational Excitations		
	$V_i$	$J_i$	$V_j$	$J_j$	$E_i$	$E_j$	$dE$	TDM	$f$	$A$
1	0	0	1	0	2051.302188863...	6013.288812386...	3961.986623522...	0.09185544234885232	1.571631048193161e-05	164.53377577085908
2	0	0	2	0	2051.302188863...	9802.4184084066	7751.116219543...	-0.01127795647202583	4.6350335909426063e-07	18.572049721835835
3	0	0	3	0	2051.302188863...	13424.30506424...	11373.00287538...	-0.0016049792884565003	1.3773421013256116e-08	1.188148092404906
4	0	0	4	0	2051.302188863...	16883.62354751...	14832.32135865...	-0.0003529206960806445	8.68542730497676e-10	0.12743475749145858
5	0	0	5	0	2051.302188863...	20183.87224469...	18132.57005583...	9.272023931627274e-05	7.328857219990254e-11	0.016070650022517754
6	0	0	6	0	2051.302188863...	23334.49262740...	21283.19043854...	-2.6743443678887942e-05	7.156475666780053e-12	0.0021619772289003464
7	0	0	7	0	2051.302188863...	26391.15393395...	24339.85174509...	-7.949563149151236e-06	7.231564512386091e-13	0.0002857239046310406
8	0	0	8	0	2051.302188863...	29527.00074670...	27475.69855784...	2.0748588666258996e-06	5.5610099752687484e-14	2.799816795611387e-05
9	0	0	9	0	2051.302188863...	32961.54139413...	30910.23920526...	-2.0595185518575397e-07	6.163985263458898e-16	3.927758508173019e-07
10	0	0	10	0	2051.302188863...	36802.04499016...	34750.74280130...	2.4129779014760206e-07	9.512585873427272e-16	7.661348692996144e-07
11	0	0	11	0	2051.302188863...	41063.45762136...	39012.1554325027	-2.3389585156438992e-07	1.0033969883176185e-15	1.0184767968899796e-06
12	0	0	12	0	2051.302188863...	45745.8518189607	43694.54963009...	1.420945094434475e-07	4.1477222888629744e-16	5.281322151506998e-07
13	0	0	13	0	2051.302188863...	50844.62131555...	48793.31912669...	7.085662178393885e-08	1.1517256952778247e-16	1.8287242917258555e-07

**Figure 5.10** First thirteen vibrational excitations using the potential energy curve of Coxon *et al.*<sup>5</sup> and the dipole moment curve of Li *et al.*<sup>6</sup>



## 5.6 Dunham Parameters Tab

The *Dunham Parameters* tab consists of a single *Refresh* button and two data tables (Figure 5.11). The *Refresh* button loads the potential energy curve information and the predicted vibrational constant from the *Power Series Expansion* tab in order to calculate the Dunham fitting coefficients (left-hand column) and the predicted Dunham parameters (right-hand column).

The Dunham polynomial expansion coefficients are shown as a function of the order and have values of  $\text{cm}^{-1}$ .

The Dunham parameters are shown as functions of the rotational (J column) and vibrational contributions (v column) as well as their spectroscopic constant equivalents (ID column).

See section 4.9 for further information.

Refresh

Dunham Coefficients

Dunham Parameters

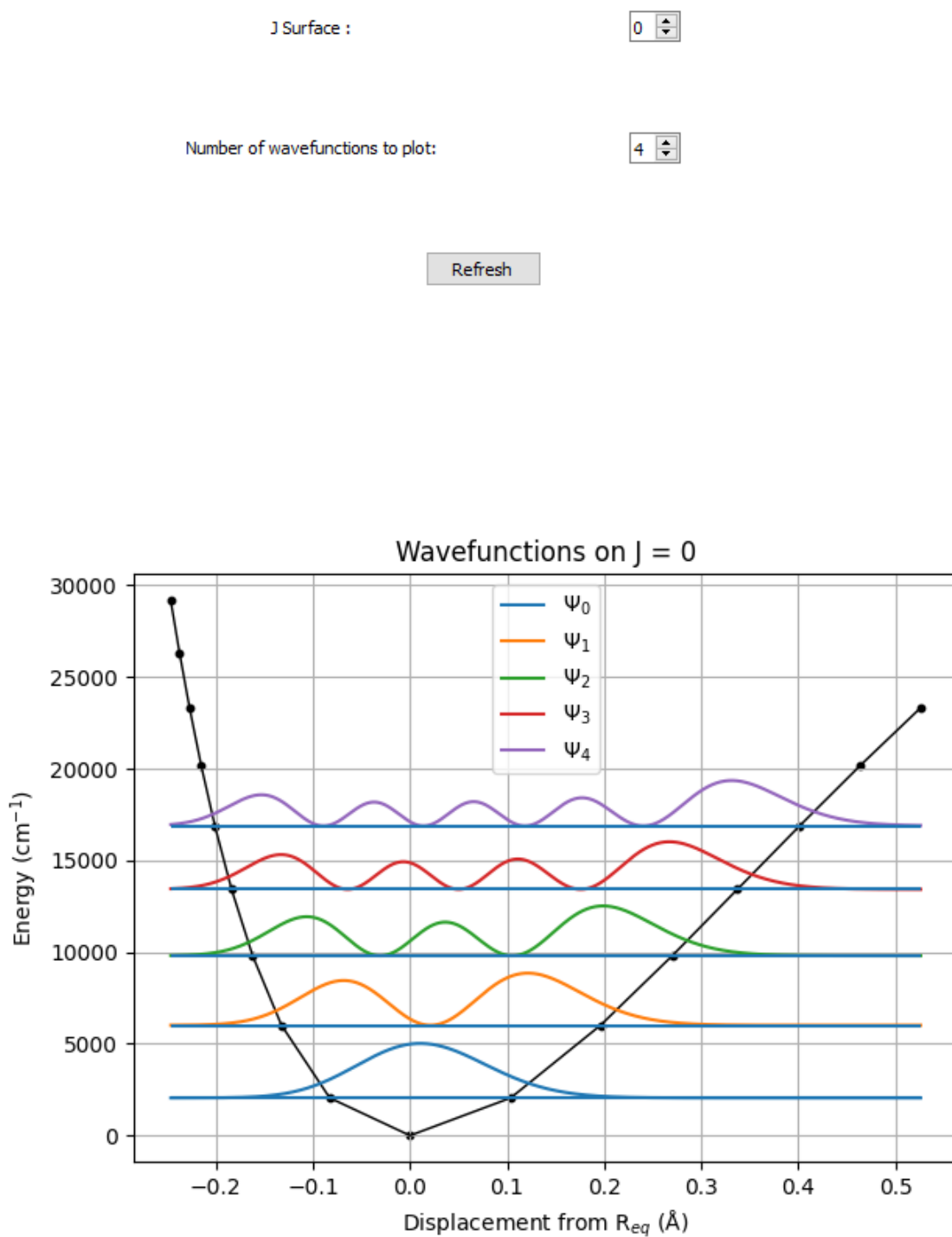
	Order	Value
1	1	-2.243643083022031
2	2	3.417500049457222
3	3	-4.499066478739045
4	4	5.631830584793634
5	5	-5.6289352343030865
6	6	2.754485017475816

	J	v	ID	Value
1	0	0	-	3.780125765343218
2	1	0	Be	20.954283248786084
3	2	0	De	-0.00214719758192023
4	3	0	He	1.6649367273252914e-07
5	4	0	Fe	-1.615514457823557e-11
6	0	1	we	4139.697242290569
7	1	1	alpha	-0.9870026337211745
8	2	1	beta	5.577449459690151e-05
9	3	1	-	-7.043952364561764e-09
10	4	1	-	0.0
11	0	2	wexe	-90.28355353088568
12	1	2	gamma	0.008189550591441812
13	2	2	-	-1.025129151803538e-06
14	3	2	-	0.0
15	4	2	-	0.0
16	0	3	weye	0.6977646687138639
17	1	3	-	0.0004562539176878139
18	2	3	-	0.0
19	3	3	-	0.0
20	4	3	-	0.0
21	0	4	weze	0.07101302350209433
22	1	4	-	0.0
23	2	4	-	0.0
24	3	4	-	0.0
25	4	4	-	0.0

**Figure 5.11** The *Dunham Parameters* tab showing the *Refresh* button (top), the Dunham coefficients data table (left), and the Dunham parameters data table (right) using the potential energy curve of Coxon *et al.*<sup>5</sup>

## 5.7 Wavefunctions Tab

The *Wavefunctions* tab allows the user to visualize the vibrational wave functions for a given system. It consists of a click box to control the specific J-surface, a click box to control the number of wavefunctions to plot, a *Refresh* button, and the wavefunction plot (Figure 5.12). The number of wavefunctions that can be plotted is either controlled by the size of the total Hamiltonian matrix or by the number of converged vibrational states based on the truncation error (see section 5.3 and 4.4.6). The *Refresh* button loads the total Hamiltonian matrix from the *Vibrational Hamiltonian* tab in order to plot the vibrational wave functions. The anharmonic wavefunctions are calculated as linear combinations of harmonic wavefunctions using the eigenvectors for each vibrational state.

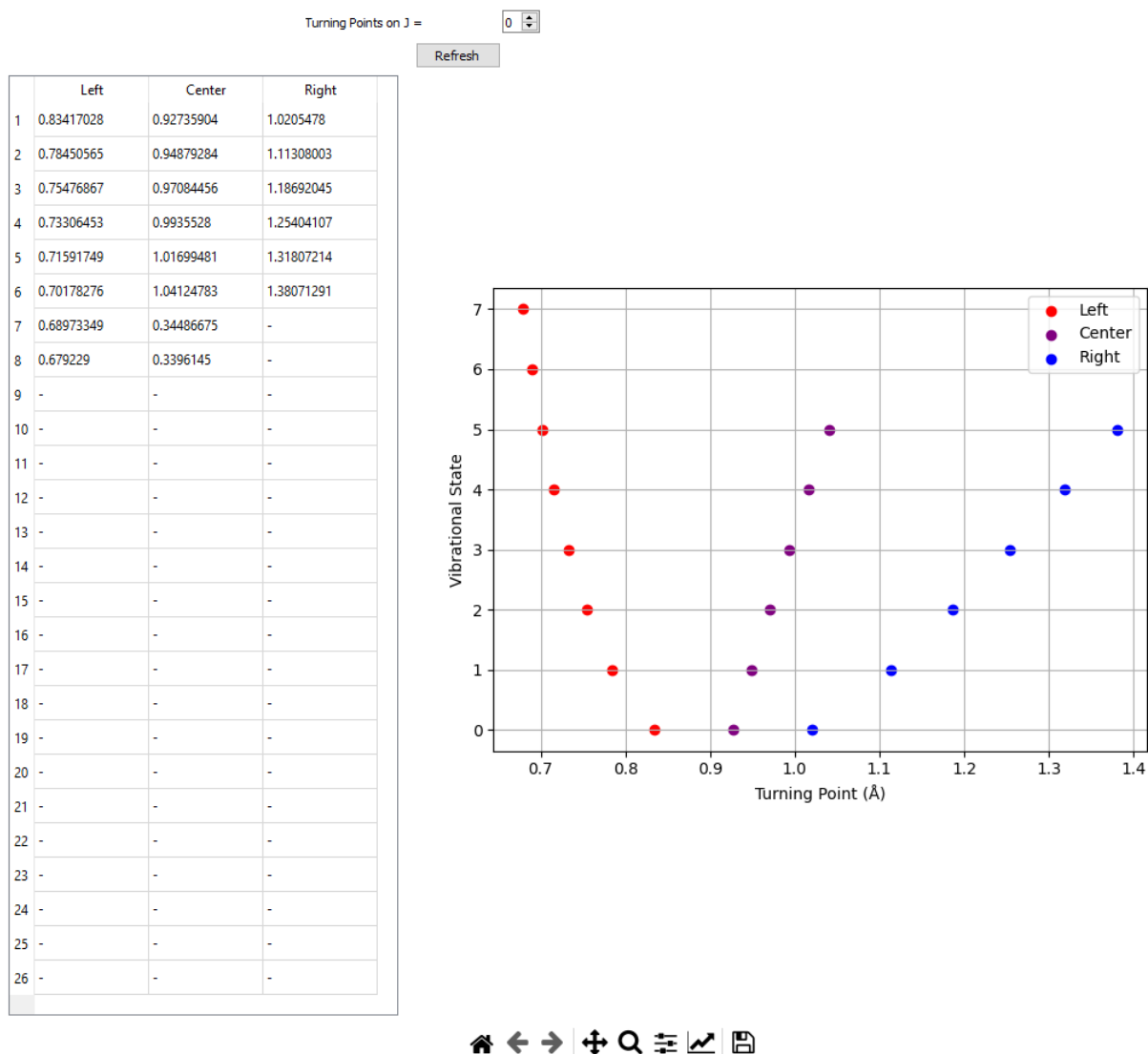


**Figure 5.12** The *Wavefunctions* tab showing the choice in the J-surface (top), the choice in the number of wavefunctions to plot (second from the top), the *Refresh* button (second from the bottom), and the plot of the wavefunction (bottom) using the potential energy curve of Coxon *et al.*<sup>5</sup>

## 5.8 Turning Points Tab

The *Turning Points* tab is used to calculate and plot the classical turning points for the potential energy curve on different J-surfaces (Figure 5.13). This tab allows the user to change the J-surface using a click box and *Refresh* the information related to the potential energy curve and the total Hamiltonian matrix. The data table on the left of the tab lists the left and right turning point values (in Å) and the center point between the two turning points. The plot to the right displays the same information shown in the data table. Only turning points which fall within the bounds of the given potential energy curve are calculated due to the inherit error that may arise outside of the interpolated region.

See section 4.5 for further information.



**Figure 5.13** The *Turning Points* tab showing the choice in the J-surface (top), the *Refresh* button (middle), and the data table listing the turning points (left), and the plot of the turning points (right) using the potential energy curve of Coxon *et al.*<sup>5</sup>

## 5.9 Simulated Spectra Tab

The *Simulated Spectra* tab contains three columns of objects relevant to pure vibrational spectra (left column), pure rotational spectra (center column), or rovibrational spectra (right column). Each column has the option to plot the population of each state using a Boltzmann distribution or to plot the intensity of each possible transition. The latter combines the calculated population values and the calculated Einstein A coefficients to arrive at the intensity value.

At the top of the screen is an area where the user can define the temperature in Kelvin for the simulated spectra. Below that is a *Refresh* button that will reload the eigenvalue information from the total Hamiltonian matrix.

The left-most column controls the plotting of pure vibrational spectra and contains eight objects:

The *Rotational Surface* click box controls the particular J-surface that is desired for plotting. These values range from -1 to the maximum J-value defined in the *Vibrational Hamiltonian* tab.

The *Maximum  $\nu$  States* click box controls how many vibrational states to include in the calculation of the Boltzmann distribution. These values range from 0 to the maximum vibrational state given either the size of the total Hamiltonian matrix or the truncation error (see section 4.4.6).

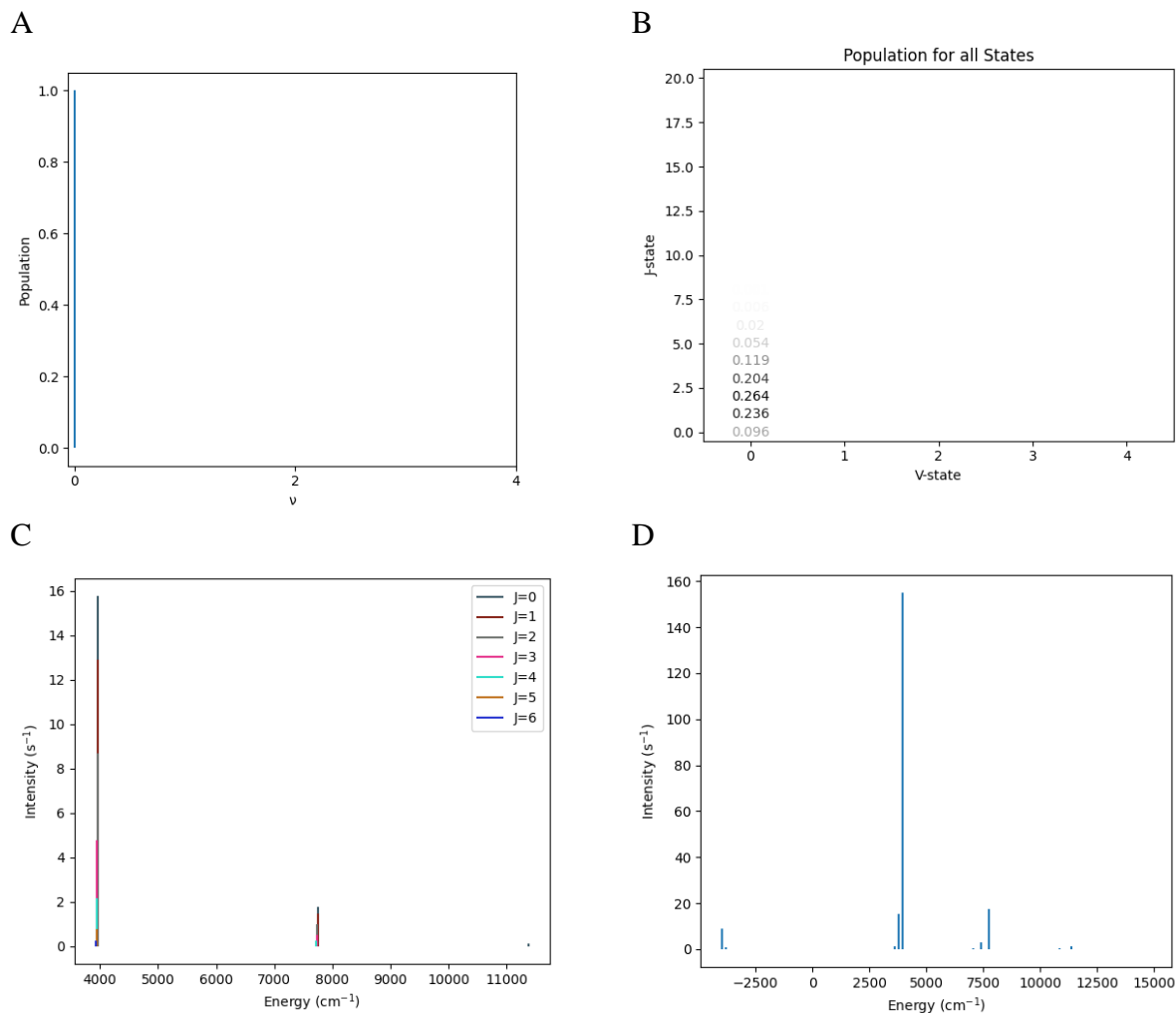
The *Plotting Cutoff* value controls the minimum population or intensity value that is included in the plot. This is included so that incredibly small values are less likely to lead to a poor looking plot.

The plot below the *Plotting Cutoff* value displays either the population information for different vibrational states or the intensity of different vibrational transitions. The choice of which to plot is included below using two radio buttons labelled *Population* and *Intensity*.

The *View Datatable* button opens an external data table that displays the information presenting in the above plot. The data table is not controlled by the *Plotting cutoff* value and so populations on all vibrational states or all vibrational transitions are included.

At temperature ranges  $< 1000$  K, only the  $\nu = 0$  state is populated to a significant amount and so only one vertical line is observed in the plot (Figure 5.14a). Increasing the temperature, however, changes the population and so more vertical lines are visible in the plot. If the user chooses a value of -1 for the *Rotational Surface* click box and the population radio button is checked, then a pseudo-heatmap plot is generated which displays the population of each vibrational state on all of the rotational surfaces (Figure 5.14b). The color of the printed text is scaled so that the highest value is in black while the lowest value is in white (and is therefore unseen). This plot is not controlled by the *Plotting Cutoff* value. For a value of -1 for the *Rotational Surface* click box with the *Intensity* radio button clicked, rovibrational spectra is plotted as a function of the different J-

surfaces (Figure 5.14c). The plot shows a legend of different “J=#” values with different colors. At elevated temperature, more vibrational states are possible and so the simulated vibrational spectra includes more transitions (Figure 5.14d).



**Figure 5.14** A) The population of vibrational states up to  $v = 4$  on the  $J = 0$  rotational surface at 298K using the potential energy curve of Coxon *et al.*<sup>5</sup> B) The population of all rovibrational states up to  $v = 4$  and  $J = 20$  at 298K using the potential energy curve of Coxon *et al.*<sup>5</sup> C) Intensity values for all vibrational excitations up to  $v = 3$  and  $J = 6$  at 298 K using the potential energy curve of Coxon *et al.*<sup>5</sup> and the dipole moment curve of Li *et al.*<sup>6</sup> D) Intensity values for vibrational excitations up to  $v = 6$  on the  $J = 0$  surface at 2000 K using the potential energy curve of Coxon *et al.*<sup>5</sup> and the dipole moment curve of Li *et al.*<sup>6</sup>



The center column controls the plotting of pure rotational spectra and contains eight objects:

The *Vibrational Surface* click box controls the particular v-surface that is desired for plotting. These values range from -1 to the maximum v-value defined in the *Vibrational Hamiltonian* tab either through the size of the total Hamiltonian matrix or the truncation error (see section 4.4.6).

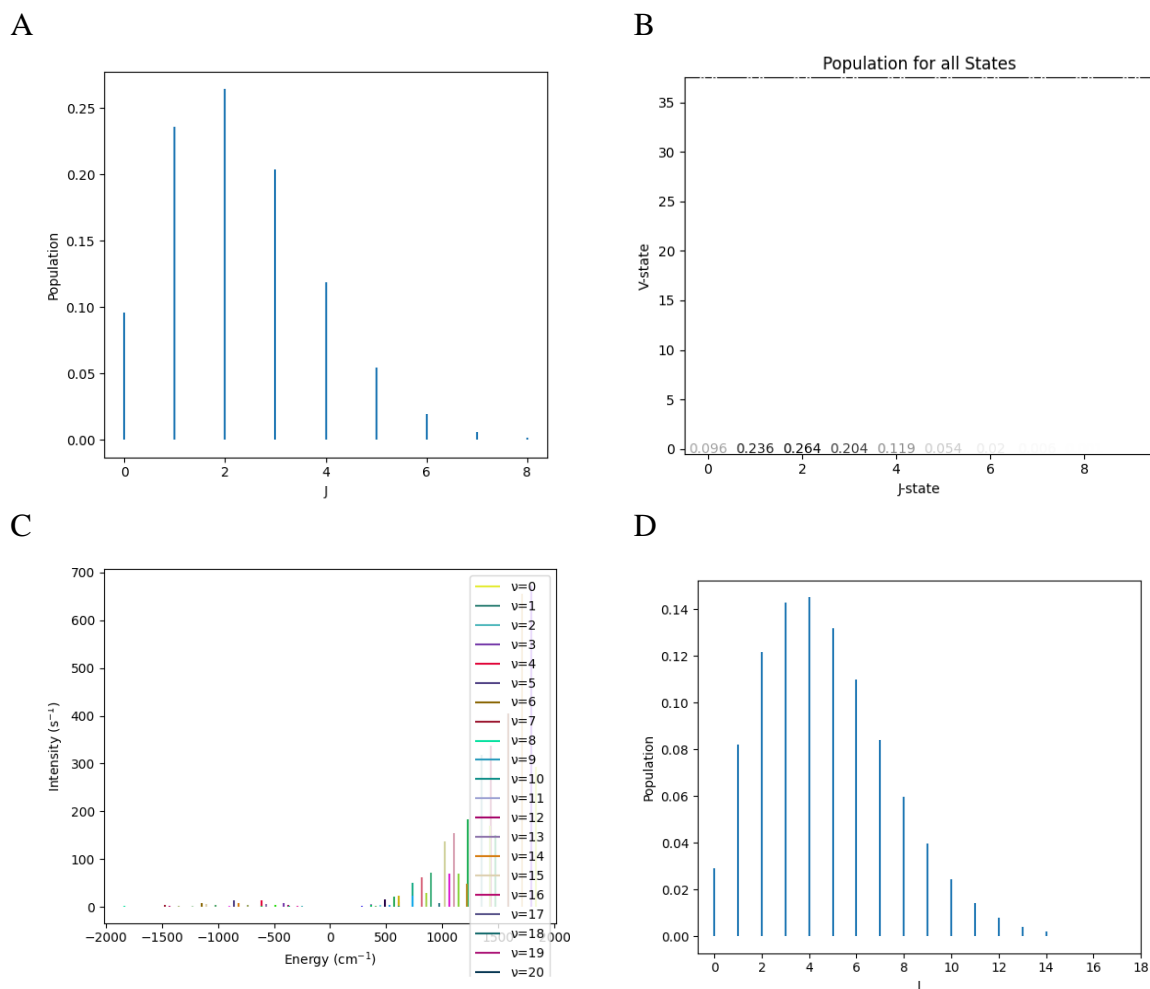
The *Maximum J States* click box controls how many rotational states to include in the calculation of the Boltzmann distribution. These values range from 0 to the maximum rotational quantum number given in the *Vibrational Hamiltonian* tab (see section 4.4.6).

The *Plotting Cutoff* value controls the minimum population or intensity value that is included in the plot. This is included so that incredibly small values are less likely to lead to a poor looking plot.

The plot below the *Plotting Cutoff* value displays either the population information for different rotational states or the intensity of different rotational transitions. The choice of which to plot is included below using two radio buttons labelled *Population* and *Intensity*.

The *View Datatable* button opens an external data table that displays the information presenting in the above plot. The data table is not controlled by the *Plotting cutoff* value and so populations on all rotational states or all rotational transitions are included.

At a temperature of 298 K, several rotational states are populated for the HF diatomic molecule (Figure 5.15a). Just as with the vibrational column, if the user chooses a value of -1 for the *Vibrational Surface* click box for a population plot, then a pseudo-heatmap is plotted which is similar to that of the vibrational case except the axes have been interchanged (Figure 5.15b). The color of the printed text is scaled so that the highest value is in black while the lowest value is in white (and is therefore unseen). This plot is not controlled by the *Plotting Cutoff* value. For a value of -1 for the *Vibrational Surface* click box with the *Intensity* radio button clicked, rovibrational spectra is plotted as a function of the different v-surfaces (Figure 5.15c). The plot shows a legend of different “v=#” values with different colors. At elevated temperature, more rotational states are possible and so the simulated vibrational spectra includes more transitions (Figure 5.15d).



**Figure 5.15** A) The population of rotational states up to  $J = 8$  on the  $v = 0$  vibrational surface at 298K using the potential energy curve of Coxon *et al.*<sup>5</sup> B) The population of all rovibrational states up to  $v = 37$  and  $J = 10$  at 298K using the potential energy curve of Coxon *et al.*<sup>5</sup> C) Intensity values for all vibrational excitations up to  $v = 20$  and  $J = 10$  at 298 K using the potential energy curve of Coxon *et al.*<sup>5</sup> and the dipole moment curve of Li *et al.*<sup>6</sup> D) Intensity values for rotational excitations up to  $J = 20$  on the  $v = 0$  surface at 1000 K using the potential energy curve of Coxon *et al.*<sup>5</sup> and the dipole moment curve of Li *et al.*<sup>6</sup>

The right-most column controls the plotting of rovibrational spectra and contains eight objects:

The *Maximum J Value* click box controls how many rotational states to include in the calculation of the Boltzmann distribution. These values range from 0 to the maximum rotational quantum number given in the *Vibrational Hamiltonian* tab (see section 4.4.6).

The *Maximum V Value* click box controls how many vibrational states to include in the calculation of the Boltzmann distribution. These values range from 0 to either the maximum vibrational quantum number given in the *Vibrational Hamiltonian* tab or the maximum truncation value (see section 4.4.6).

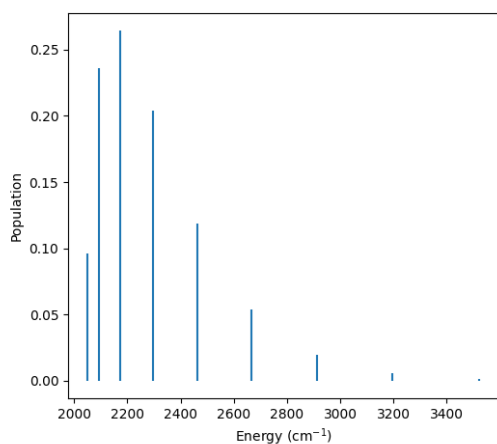
The *Plotting Cutoff* value controls the minimum population or intensity value that is included in the plot. This is included so that incredibly small values are less likely to lead to a poor looking plot.

The plot below the *Plotting Cutoff* value displays either the population information for different rovibrational states or the intensity of different rovibrational transitions. The choice of which to plot is included below using two radio buttons labelled *Population* and *Intensity*.

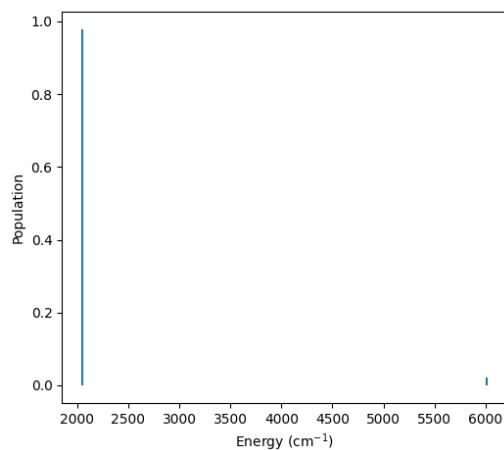
The *View Datatable* button opens an external data table that displays the information presenting in the above plot. The data table is not controlled by the *Plotting cutoff* value and so populations on all rotational states or all rotational transitions are included.

The rovibrational plots can resemble pure vibrational spectra if the *Maximum J Value* click box is set to 0 (Figure 5.16a) or pure rotational spectra if the *Maximum V Value* click box is set to 0 (Figure 5.16b). The resulting rovibrational spectra is no labelled according to the rotational or vibrational state (Figure 5.16c) but does resemble the vibrational spectra observed in the left-hand plot. At elevated temperatures, many rovibrational excitations are possible with significant intensity values (Figure 5.16d).

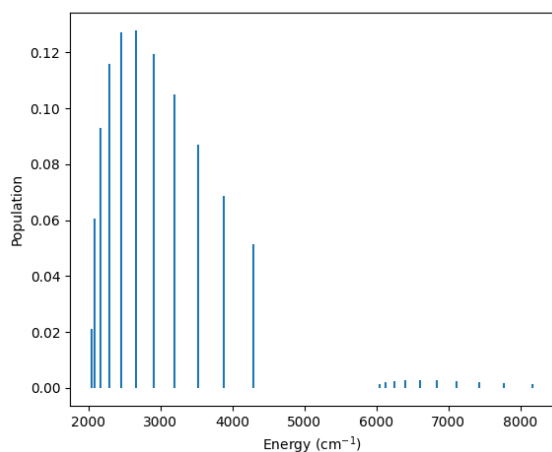
A



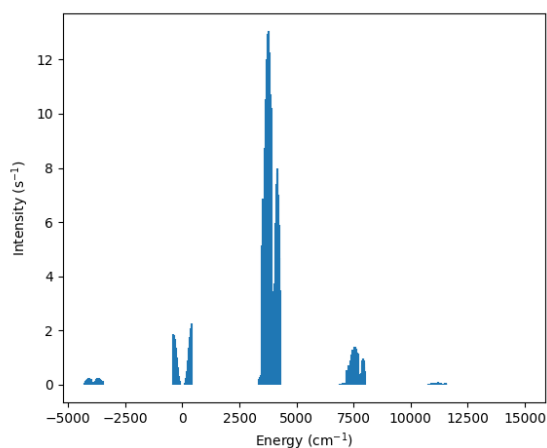
B



C



D



**Figure 5.16** A) The population of pure rotational states up to  $J = 10$  on the  $v = 0$  vibrational surface at 298 K using the potential energy curve of Coxon *et al.*<sup>5</sup> B) The population of pure vibrational states up to  $v = 4$  and  $J = 0$  at 1500 K using the potential energy curve of Coxon *et al.*<sup>5</sup> C) The population of rovibrational states  $v = 4$  and  $J = 10$  at 1500 K using the potential energy curve of Coxon *et al.*<sup>5</sup> D) Intensity values for rovibrational excitations up to  $J = 10$  and  $v = 4$  at 1500 K using the potential energy curve of Coxon *et al.*<sup>5</sup> and the dipole moment curve of Li *et al.*<sup>6</sup>

## 6 Some Tips & Tricks

The generation of the anharmonic and centrifugal potential Hamiltonian matrices is very computationally demanding. As such, the program will freeze momentarily while the matrices are being constructed. This behavior will be fixed in future updates.

The accuracy of the predicted spectra and spectroscopic values is very dependent on three things: the quality of the initial potential energy and dipole moment curves, the accuracy of the interpolated curves, and the size of the Hamiltonian matrices. For the first point, calculations performed at low levels of electronic structure theory (EST) such as Hartree-Fock (HF) or density functional theory (DFT) can result in poor quality energy and dipole curves. Because of this, any results obtained using the VibHam program must be accompanied with the chosen level of theory; the results of VibHam are only as good as the given curves. With regards to the second point, the equilibrium bond length, minimum energy, and initial vibrational constant are highly dependent on the number of interpolation points used in the *Power Series Expansion* tab. A finer grid of interpolation points results in a higher accuracy prediction for those three values. And finally, the choice in the size of the Hamiltonian matrix is one that must be considered carefully. A larger Hamiltonian matrix will result in more converged states but at the cost of more computational resources. The construction of the Hamiltonian matrices has a computational cost of  $O(n^2)$  where  $n$  is the maximum vibrational quantum number and so larger matrices will require a higher computational effort.

## 7 Publications Related to VibHam

- (1) McCarver, Gavin A.; Hinde, Robert J. “VibHam: An Efficient Program for Predicting Rovibrational Spectra of Diatomic Molecules” *in preparation*
- (2) McCarver, Gavin A.; Hinde, Robert J. “Improved Potential Energy Curves and Dipole Moment Functions for the  $X^1\Sigma^+$  and  $a^3\Pi$  spin states of the  $CF^+$  Diatomic Molecule” *in preparation*
- (3) McCarver, Gavin A.; Hinde, Robert J. “Filling in the Gaps: Spectroscopic Constants for Lanthanide Diatomics Computed using Theoretical Methods” *in preparation*
- (4) McCarver, Gavin A.; Hinde, Robert J. “The Effect of Full Triple Excitations on the Prediction of Spectroscopic Constants for Single- and Multireference Diatomic Molecules” *in preparation*

## Bibliography

- (1) Shi, D. H.; Li, W. T.; Sun, J. F.; Zhu, Z. L. Theoretical Study of Spectroscopic and Molecular Properties of Several Low-Lying Electronic States of CO Molecule. *Int. J. Quantum Chem.* **2013**, *113* (7), 934–942. <https://doi.org/10.1002/qua.24036>.
- (2) Rank, D. H.; Pierre, A. G. St.; Wiggins, T. A. Rotational and Vibration Constants of CO. *J. Mol. Spectrosc.* **1965**, *18*, 418–427.
- (3) Londoño, B. E.; Mahecha, J. E.; Luc-Koenig, E.; Crubellier, A. Shape Resonances in Ground-State Diatomic Molecules: General Trends and the Example of RbCs. *Phys. Rev. A - At. Mol. Opt. Phys.* **2010**, *82* (1), 1–15. <https://doi.org/10.1103/PhysRevA.82.012510>.
- (4) Hansson, A.; Watson, J. K. G. A Comment on Hönl-London Factors. *J. Mol. Spectrosc.* **2005**, *233* (2), 169–173. <https://doi.org/10.1016/j.jms.2005.06.009>.
- (5) Coxon, J. A.; Hajigeorgiou, P. G. Improved Direct Potential Fit Analyses for the Ground Electronic States of the Hydrogen Halides: HF/DF/TF, HCl/DCI/TCI, HBr/DBr/TBr and HI/DI/TI. *J. Quant. Spectrosc. Radiat. Transf.* **2015**, *151*, 133–154. <https://doi.org/10.1016/j.jqsrt.2014.08.028>.
- (6) Li, G.; Gordon, I. E.; Le Roy, R. J.; Hajigeorgiou, P. G.; Coxon, J. A.; Bernath, P. F.; Rothman, L. S. Reference Spectroscopic Data for Hydrogen Halides. Part I: Construction and Validation of the Ro-Vibrational Dipole Moment Functions. *J. Quant. Spectrosc. Radiat. Transf.* **2013**, *121*, 78–90. <https://doi.org/10.1016/j.jqsrt.2013.02.005>.
- (7) Dunham, J. L. The Energy Levels of a Rotating Vibrator. *Phys. Rev.* **1932**, *41*, 721–731. [https://doi.org/10.1016/0375-9474\(74\)90152-3](https://doi.org/10.1016/0375-9474(74)90152-3).